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DEVELOPMENT OF A TEST METHOD FOR THE DETERMINATION OF THE HYDROPEROXIDE POTENTIAL AND ANTIOXIDANT EFFECTIVENESS IN JET FUELS DURING LONG TERM STORAGE

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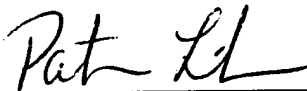USING GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATE INCLUDED IN THIS DOCUMENT FOR ANY OTHER PURPOSE OTHER THAN GOVERNMENT PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE US GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL, ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

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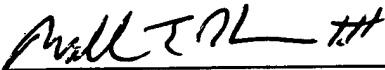
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A reliable test method is needed for predicting the long term storage stabilities of military aviation turbine fuel reserves as well as for evaluating the effectiveness of antioxidants approved for these fuels. This report addresses this need. It describes a reliable and practical accelerated test method for predicting the peroxidation potential of aviation turbine fuels that are stored for long term periods. A test methodology is also proposed for evaluating antioxidants for future qualification in the military specification, MIL-T-5624. This paper is based on the collective results of extensive rigorous studies performed by the four participating laboratories: Southwest Research Institute (SwRI), San Antonio, Texas; Naval Research Laboratory (NRL) Washington, D.C.; Naval Air Warfare Center (NAWC), Trenton, New Jersey; and the National Institute of Petroleum and Energy Research (NIPER), Bartlesville, Oklahoma.

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A-1 EXECUTIVE SUMMARY

A reliable test method is needed for predicting the long term storage stabilities of military aviation turbine fuel reserves as well as for evaluating the effectiveness of antioxidants approved for these fuels. This report addresses this need. It describes a reliable and practical accelerated test method for predicting the peroxidation potential of aviation turbine fuels that are stored for long term periods. A test methodology is also proposed for evaluating antioxidants for future qualification in the military specification, MIL-T-5624. This paper is based on the collective results of extensive rigorous studies performed by the four participating laboratories: Southwest Research Institute (SwRI), San Antonio, Texas; Naval Research Laboratory (NRL) Washington, D.C.; Naval Air Warfare Center (NAWC), Trenton, New Jersey; and the National Institute of Petroleum and Energy Research (NIPER), Bartlesville, Oklahoma.

The proposed accelerated test method for predicting the long term storage stabilities of JP-5 fuels entails conducting the stress test in a Low Pressure Reactor (LPR) at 100°C stress temperature, and 50 psia (344.8 kPa) overpressure air for 24 hours with the option to extend to 48 hours if deemed necessary. The 100°C stress temperature has been validated to be predictive of long term storage at ambient conditions. The use of 50 psia air overpressure appears to be ample in preventing oxygen depletion at this elevated temperature and test duration. The reactor of choice is the LPR designed by the Naval Research Laboratory. Use of the method to determine the long term storage stabilities of worldwide current production fuels suggests the 24-48 hour test duration to be adequate in differentiating fuels with differing stabilities, with and without hindered phenol antioxidants. The 100°C/24 hour stress test simulates approximately nine months storage at ambient conditions and meets the Navy's protocol for periodic testing on a six-month basis. Studies that extended the stress test duration to 96 hours confirm the need for periodic testings.

Prior to the development of the above test method, various accelerated stress tests were used to evaluate the effectiveness of 13 antioxidants listed in MIL-T-5624L specification. These tests indicate that antioxidant effectiveness is dependent on its structure, the stress test conditions, and the test fuel. Recommendations for the future qualification of antioxidants for aviation turbine fuels include the following: (a) adopt the proposed 100°C accelerated stress temperature and 50 psia air overpressure; (b) conduct tests at a minimum of three stress periods (24, 48, and 96 hours); (c) select fuels of poor, marginal, and good storage stabilities, as defined in this paper; and (d) evaluate relative antioxidant effectiveness on the magnitude of the stress time for which the 8.0 ppm peroxide number specification limit is not exceeded relative to the corresponding neat fuel and to a reference antioxidant.

B-1.0 Part 1: Test Method Development

B-1.1 INTRODUCTION

To ensure combat readiness of the fleet in worldwide operations, the U.S. Navy maintains large strategic reserves of fuels which are stored in locations of diverse climatic conditions for extended time periods. This report addresses the long term storage stability assurance of aviation turbine fuels. Specifically, it is the Navy's position paper on a reliable and practical accelerated test method for predicting the peroxidation potential of aviation turbine fuels, i.e., the potential to form hydroperoxides during long term storage. An overall evaluation of 13 antioxidants that were approved in the military specification, MIL-T-5624L, for aviation turbine fuels' storage stability is also presented, and recommendations are proposed for future qualification testings.

Like other hydrocarbon-based fuels, aviation turbine fuels are susceptible to autoxidation during long term storage. The resultant reaction products of primary concern are hydroperoxides. These products have been found to be detrimental to the elastomers in aircraft fuel systems (*see* below). The formation of other autoxidation products during storage, viz., gums and sediments are not directly addressed in this paper, since these products are ultimately controlled by the hydroperoxide levels. Cited cases of fuel pump failures that have been attributed to the fuel's hydroperoxide level follow.

The first reported failures[1] occurred in Japan in 1962. Specifically, flexible fuel manifold hoses in Rolls Royce Dart engines, operating in the Far East, cracked and leaked. These hoses were made of neoprene or nitrile rubbers; likewise, were the rubber sealing rings and diaphragms in the fuel control system, which were also affected, but to a lesser extent. The fuel employed was a Jet A-1 and the hydroperoxide levels (peroxide number) associated with this incident were 16-40 ppm (2-5 meq/kg: milli-equivalents of active oxygen/kilogram of fuel).[2] In response to this occurrence, the UK Directorate of Engine Research and Development (DERD) specification 2494 was revised to require the addition of approved oxidation inhibitors to all hydrotreated stocks.[3]

In the Spring of 1976, the U.S. Navy experienced compressor stalls in an A-7E aircraft operating out of the Philippines.[4] The stalls resulted from failure of a neoprene fuel pump diaphragm used in the TF41-A-2 engine. The fuel employed was a JP-5 and its peroxide numbers at the time of the incident were 8-64 ppm (1-8 meq/kg).[2] To minimize future problems, specification MIL-T-5624K was amended in November 1976 to require the addition of oxidation inhibitors to all JP-5 fuels and to JP-4 fuels containing hydrotreated stocks.[3] Also, in response to the Philippine's problem, the U.S. Navy set a maximum peroxide number specification of 8.0 ppm (1 meq/kg).[3]

An additional case in point, on the need for antioxidants, is the fuel pump leak that was reported by the Royal Thai Air Force in 1984.[3] The leak had resulted from cracks in the Buna-N O-rings and the fuel employed was a JP-4 that did not contain an antioxidant. Its peroxide

numbers during this problem were 16-32 ppm (2-4meq/kg).[2] Subsequent use of antioxidants and a change in the elastomers resulted in no further problems.[3] Nonetheless, these cited cases of fuel pump failures focus on the significance of fuel peroxidation since it impacts on strategic and economic costs to the military, e.g., safety/survivability, downtime, and fuel downgrading.

The peroxidation potential of aviation turbine fuels is further exacerbated by the projected decreasing quality of future crudes, which will be heavier, and/or contain more sulfur. This problem is compounded by increasing demands for transportation fuels. Consequently, more severe processing is required. For example: hydrotreating, to upgrade fuel quality; and cracking, to maximize fuel yields from the bottom of the barrel. Furthermore, hydrotreatment can destroy naturally occurring inhibitors, and cracked stocks contain more unsaturated components (particularly olefins including cyclic and aromatic olefins), as well as more more branched chain compounds and heterocompounds. Most of these compounds are susceptible to oxidation and are therefore less stable.

To meet the need for storage-stable aviation turbine fuels, the Navy's approach to mandate the use of antioxidants has been successful (*see* above). However, antioxidant shortages in 1974, highlighted the demand for a procedure that identified hydroperoxide-forming fuels. The available ASTM D3703 test method measures only the *existent* hydroperoxide concentration. Consequently, a test method that would reliably *predict* the peroxidation potential of aviation turbine fuels was sought. In response to this quest, in 1980, the Coordinating Research Council (CRC) Group on Oxidation Stability of Jet Fuels formed the Hydroperoxide Potential of Jet Fuels Panel, to develop such a procedure. The studies performed are documented in a CRC Report.[3] Nevertheless, for completeness in reviewing the development of the Navy's accelerated predictive test method, these earlier studies are summarized below.

Preliminary Tests: The preliminary development of an accelerated test method to predict the peroxidation potential of aviation turbine fuels was conducted at the Naval Research Laboratory (NRL). Nineteen fuels were tested (*see* Table 1). The test procedure was based on a Rolls Royce experience in the 1960s,[5] and is as follows: The sample (250 mL), contained in a clean amber *capped* borosilicate bottle (500 mL), was stressed at 100°C in an explosion proof oven; periodically, the bottle was removed from the oven, cooled, and analyzed for hydroperoxide content based on the ASTM D1563 method. Conclusions of this study were that the test method gave reasonable repeatability and distinguished between different samples. In addition, antioxidants were noted to inhibit peroxidation of petroleum-derived fuels, but not that of shale-derived fuels.

CRC Cooperative Test Programs: Three Round Robin studies were conducted during 1982-1987. The results of each study were used with the intent towards improving the test method. The revisions adopted in the third round robin (CRC 3) include aeration of the sample prior to testing, and loosely-capped bottle tests - to obviate oxygen depletion. However, the decision not to further examine the use of temperatures >65°C was proven by later testings to be incorrect. The three CRC studies are subsequently described and to better discern the various modifications, the

revisions in the test procedure are tabulated in Table 1, and in the fuels employed, in Table 2. Further details are given in the CRC Report.[3]

The *first round robin program (CRC 1)* was in 1982 and involved duplicate testing of seven selected fuels by six laboratories. In the test procedure, the sample (350 mL) was stressed in capped 500 mL amber borosilicate bottles at 100°C for 7 days and analyzed periodically for hydroperoxides. Peroxide number was determined by ASTM D 3703-78, but with the use of Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), as the solvent, instead of carbon tetrachloride. Whereas the repeatability of the results was reported to be reasonable, the reproducibility was poor.

An additional study was conducted at NRL to examine the effect of temperature on peroxidation. The objective of this study was to investigate the relevance of peroxidation at higher temperatures with that at ambient conditions. In both CRC 1 and the initial NRL tests, the stress temperature of 100°C was employed. Test temperatures lower than 100°C, for longer periods were also examined, viz., 43°, 65°, and 80°C (see Table 1). The overall results of this study and the main CRC 1 investigation, erroneously implied a change in mechanism at 80° and 100°C stress temperatures. It was for this reason, 80° and 100°C stress temperatures were considered not to be predictive of storage at ambient conditions,[2] and subsequent round robin programs were conducted at 65°C.

In the *second round robin program (CRC 2)*, which was conducted in 1984, procedural measures were taken to lessen excessive variability of the results. Five fuels were stored at 65°C for 56 days with hydroperoxide analyses at 1, 3, 7, 14, 21, and 35 days. A major shortcoming of this study was the stability of the fuels (0.5 ppm hydroperoxides after 8 weeks at 65°C). Also, four of the five fuels contained an antioxidant.

In the *third round robin program (CRC 3)*, the fuels were carefully selected from a broader range of sources. To ensure that a majority of the fuels developed significant levels of hydroperoxides (>8 ppm), the fuels were hydrotreated and contained no antioxidants. Also, prior to testing, the test samples were first aerated and the bottles then loosely capped. At sampling time the caps were left off for 15-30 minutes. The test matrix comprised eight laboratories, nine fuels, and triplicate testings at 65°C stress temperature. The salient conclusion of the cooperative effort was that the accelerated test at 65°C for 3 weeks readily differentiates stable from unstable fuels. Thus, the method was recommended as a pass/fail test for screening the peroxidation potential of aviation turbine fuels. The repeatability and reproducibility aspects of the results however precluded its use as a quantitative tool.

Need for a Rapid Predictive Test: As a predictive tool, the 65°C/3 weeks stress test, recommended by CRC 3, is too lengthy. The ability to adequately predict the peroxidation potential of aviation turbine fuels in as short a time as possible is important particularly from: (a) the procurement aspect (especially in the case of future fuels); and (b) in the case of fuel reserves, on an ongoing basis, since antioxidants in fuels are depleted during long term storage. A reliable accelerated

stress test method is also useful for qualifying antioxidants, i.e., for determining their effectiveness with time (see Part 2).

Accordingly, the *objective* was to develop an accelerated test method that would realistically predict within 24-48 hours: (a) the peroxidation potential of aviation turbine fuels for an ambient storage period of at least six months; and (b) the effectiveness of antioxidants when added to fuels that are stored for long periods. The predictive period of at least six months is related to the Navy's current protocol, which requires the hydroperoxide levels of the fuel reserves to be analyzed at six month intervals to assure the future storage stability of its fuel reserves. Thus, the overall objective of the accelerated predictive method was that it should be realistic, and practical. The need for a rapid predictive test method prompted re-investigations at higher temperatures (>65°C). This approach was supported by Fodor *et al.* studies,[6,7] which indicated that the earlier CRC 1 results (extended study of CRC 1) were spurious - a consequence of oxygen depletion.

It is well known that fuels peroxidize slowly at ambient conditions and the rate dramatically increases at higher temperatures. The 43°C bottle test at atmospheric pressure (ASTM D4625) is generally accepted as simulating the storage of fuels at ambient temperature and pressure for long periods. The reliability of a new test method is therefore linked to establishing a similarity in the overall peroxidation mechanism between the 43°C bottle test, and accelerated storage at meaningful elevated temperatures and safe overpressures of air/oxygen for considerably shorter time periods. However, the maximum temperature that can be employed is limited because at very high temperatures (>290°C for dodecane), hydroperoxide decomposition also occurs. Additionally, in the accelerated stress test, an overpressure of air is necessary to ensure oxygen depletion of the fuel does not occur due to the increased reaction rates at higher temperatures, and possibly as an accelerator of equilibrium conditions to the peroxidation breakpoint, i.e., shortening the induction period.

This paper reports on the successful development of a test method (Part 1). And, based on an in-depth evaluation of antioxidants for the long term storage of aviation turbine fuels, a test methodology is proposed for qualifying such types of antioxidants (Part 2). Three laboratories contributed to the development of the Navy's accelerated predictive test method, viz., Southwest Research Institute (SwRI), San Antonio, Texas; the U.S. Naval Research Laboratory (NRL) Washington, D.C.; and the Naval Air Warfare Center (NAWC), Trenton, New Jersey. The participants in the evaluation of antioxidants using various accelerated stress tests were SwRI, and the National Institute for Petroleum and Energy Research (NIPER), Bartlesville, Oklahoma.

The proposed accelerated test method for predicting the peroxidation of aviation turbine fuels comprises stress conditions of: 100°C, 50 psia air overpressure for 24 hours with the option to extend to 48 hours if deemed necessary, e.g., fuels that marginally meet the 8.0 ppm specification limit. The stress duration of 100°C/24 hours is equivalent to ambient storage for approximately nine months. Such a predictive time frame amply meets the objective mentioned earlier.

B-1.2.0 EXPERIMENTAL

The validation stress tests conducted by SwRI and NRL are given in Table 3.

B-1.2.1 *Bottle tests*:

The 43 °C bottle test (ASTM D4625) is generally accepted as a reliable test method for simulating storage at ambient temperature and pressure. Bottle tests at 43°C/atmospheric pressure therefore provide a point of reference to compare the validity of accelerated tests at higher temperatures. At SwRI, these tests were conducted using a modified version of the ASTM D4625 method of bottle storage at 43°C. The modifications, which were designed to detect and correct for oxygen depletion during storage, are as follows: the test sample (300 mL, contained in a 500 mL-amber borosilicate bottle) is saturated with synthetic air (21% oxygen and 79% nitrogen) prior to stressing; the bottle is sealed during stressing, but re-aerated, when the oxygen level in the vapor phase dropped below 10.0 vol%.

The 65 °C stress tests. Based on the results of CRC 3, 65°C is recognized as an acceptable temperature for realistically predicting storage at ambient conditions. Thus, 65°C stress tests have been used as an alternative to the 43°C test by some laboratories. At SwRI, the 65°C bottle tests were conducted using the same procedure adopted in CRC 3 (Table 1).

B-1.2.2 *Pressure reactor tests*:

To ensure oxidation depletion does not occur at the higher temperatures, pressure reactors were used to conduct the accelerated stress tests at various elevated temperatures and overpressures of air and oxygen. The reactors used by SwRI,[6] and NRL are described briefly in Table 4. NRL's Low Pressure Reactor (LPR) is the same as that used in the ASTM D5304 method for assessing the storage stability of diesel fuels. For comparison, the reactor used by NIPER[8] in the antioxidants' screenings (Part 2) is included in Table 4. The stress conditions employed in the various tests by the various laboratories are, as specified, in the respective Tables. Note, as indicated in Table 4, for hydroperoxide analysis at periodic intervals, the reactor used by SwRI does not require de-pressurization for sample withdrawal. In the case of NRL's LPR and the reactor used by NIPER, the respective reactor is de-pressurized for sample withdrawal, and then immediately re-pressurized to the test overpressure.

Method used at SwRI
The reactor containing 300 mL test fuel is purged with ultra-high purity oxygen (99.99%) prior to pressurization with ultra-pure oxygen. The fuel is magnetically stirred at 150 rpm and heated to the test temperature, which is reached within 30 minutes, and timing started thereafter. To ensure reproducibility of the data, the temperature is maintained within $\pm$ 0.5°C of the desired value. The test conditions employed are given in Table 3.

Method used at NRL
The method is similar to that described in ASTM D5304 except for the stress conditions employed, which are, as noted, in the respective Tables.

B-1.2.3 *Hydroperoxide analysis*

SWRI and NIPER both used the method specified in MIL-T-5624N, viz., ASTM D3703 for determining hydroperoxide content. NRL used the potentiometric method described by Morris *et al.*[9] A distinct advantage of the potentiometric method versus D3703 (a colorimetric method) is the accuracy of the endpoint detection.

B-1.3.0 RESULTS AND DISCUSSION
B-1.3.1 **Validation of accelerated stress tests**
B-1.3.1.1 *SwRI Studies*

Fodor *et al.*,[6,7,10-12] at SwRI, conducted extensive studies that validate the use of accelerated stress conditions in conjunction with an overpressure of air/oxygen for predicting long term storage at ambient conditions. The temperature/time studies of the accelerated stress tests performed, i.e., greater than 43° or 65°C, were generally equivalent to a range of approximately 6-9 months to 1.5 years storage time at ambient conditions. The test matrix comprised: ten fuels of diverse processing/treatment (Table 5), five temperatures (43°, 65°, 80°, 100°, and 120°C), and four levels of air/oxygen overpressure: atmospheric (101 kPa air); and 240 kPa (34.8 psia), 790 kPa (114.5 psia), and 1140 kPa (165.3 psia) oxygen. As shown in Table 3, not all the temperatures and overpressures were examined for all the fuels. For validation purposes, stress tests at 43° or 65°C temperature and atmospheric pressure were included in most cases.

The thorough and extensive validation studies of Fodor *et al.* have been reported in detail as Interim[6,7] and Final reports[12] as well as published/presented elsewhere.[10,11] For this reason, this paper highlights only the results of the validation studies, i.e., the similarity in the mechanism at 43°C with that at higher temperatures and overpressures of air/oxygen (Table 6). The criterion for validation, and the ensuing results are given below.

Criterion: The criterion for validating the use of accelerated temperatures and short stress times to simulate long term storage stability at ambient conditions is based on the following: an Arrhenius plot of ln k versus 1/T should give a straight line, where k is the rate of peroxidation and T, the temperature in kelvin.

Results. In the linear regression analyses of the Arrhenius plots, the high degree of fit of the data for *each* of the ten fuels examined (R^2 = 0.97 and above, *see* Table 6) attests to the similarity in the peroxidation mechanism at accelerated temperatures. This validation of a similarity in the mechanism at ambient conditions versus accelerated storage conditions is particularly sound for eight of the ten test fuels for the following reason: their peroxidation rate data include tests
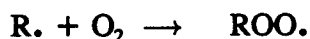
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conducted at elevated temperatures/overpressures of oxygen, and at either 43° or 65°C stress temperatures/atmospheric pressure. The stress tests of the remaining two fuels, #18496 and #18497, however, do not include 43° or 65°C stress temperatures (*see* Table 3, SwRI studies).

Activation Energy (E_a is derived from the slope of the Arrhenius plot). The activation energies for the ten test fuels ranged from 19-30 kcal/mole (Table 6). This range, though seemingly large, should not, however, dispute the above validation results since the peroxidation of fuels is the net result of competing sets of reactions of a complex mixture of compounds as indicated below:

(1) Peroxidation is not a single reaction, but the net result of competing reactions, which include the following well-known initiation, propagation, and termination reactions, where R. is a great variety and number of species:

R-H + I (initiator) ⟶ R. + IH   *Initiation*

R. + O_2 ⟶ ROO.   *Propagation*

ROO. + R-H ⟶ ROOH + R.

ROO. + R*CHOO.R** ⟶ ROH + R*COR** + O_2 *Termination*
(*i.e.*, for R* group with an alpha-hydrogen)

ROO. + R. ⟶ ROOR

R. + R. ⟶ R-R
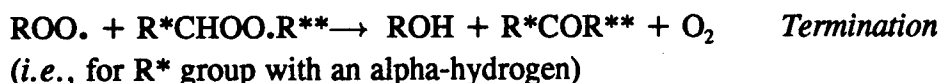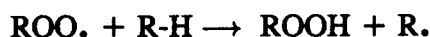
(2) Fuels are composed of a complex mixture of hydrocarbons, *viz.*, the bulk components, and polar compounds, *viz.*, the trace components. Depending on the fuel, these components can differ both in percentage and type. Specifically, the hydrocarbons in fuels comprise straight chain, branched chain, and cyclo paraffins, olefins, and monocyclic and dicyclic aromatics. Of these compounds, olefins, tertiary hydrocarbons, and aromatics are particularly susceptible to peroxidation. To address such problems, the military specification for aviation turbine fuels (MIL-T-5624) has limited the olefin content to a maximum of 5% by volume. The specification limit of the total aromatics content to a maximum of 25%, by volume, is likewise advantageous. Fuels may also contain trace amounts of naturally occurring polar compounds which can inhibit or promote autoxidation. Such components include oxygen, nitrogen, and sulfur containing compounds.

Analysis of the E_a values for the ten test fuels indicates that the overall E_a range can be subdivided into two smaller ranges, viz., 19-23, and 24-30 kcal/mole. The E_a value appears to depend on either the fuel, or its degree of peroxidation, or both (Table 6). Examples of differences in E_a for the same fuel - apparently attributable to the degree of peroxidation or fuel treatment, are cited below.

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(a) Induction versus post induction period: Four of the ten test fuels appear to exhibit this E_a range difference between their induction and post induction periods. For these fuels, the higher range appears to be associated with the induction period which may be attributable to an inhibitor that is inherently present. Thus the rate of peroxidation is lower and the E_a is higher. As the inhibitor is depleted with time, the peroxidation rate increases and hence the E_a value is lower.

(b) Alumina treated versus non treated fuel: The two alumina treated fuels appear to exhibit similar E_a values. The lower E_a value for the alumina-treated versus the non-treated fuel (#11381) suggests the removal of acidic type inhibitors. This is consistent with the literature[13a] that acidic species can act as hydroperoxide decomposers. Some increase in hydroperoxide formation, on alumina treatment of two stable fuels, was also found by Black and Hardy.[14]

B-1.3.1.2 *NRL Studies*

At NRL, Black and Hardy conducted several studies[15-17] that confirm SwRI's results.[10-12] NRL's studies include the following:

(1) *Need for adequate oxygenation of fuels on accelerated storage.* Table 7 shows the hydroperoxide concentrations formed in capped versus vented bottle tests for five fuels stressed for 12 weeks at 65°C/atmospheric pressure. These results clearly indicate that under the same stress test conditions, for three of the five fuels examined, the hydroperoxide concentrations were significantly lower (27-74 fold) in the capped versus the vented bottles.[15,16] Graphic representations of the hydroperoxide concentration with stress duration (Figures 1 and 2), further illustrate this point. Note the magnitude of the ordinate is significantly larger for the vented bottles than for the capped. In the bottle storage tests at 43°C, Fodor *et al.*[12] found the oxygen that is depleted in the liquid phase is apparently replenished by oxygen in the vapor phase.

NRL's results along with those of SwRI[10-12] focus on: (a) the importance of adequate oxygenation in accelerated stress tests - particularly for those fuels that are susceptible to peroxidation; and (b) the spurious implications that can ensue as a consequence of oxygen depletion in capped-bottle tests. Thus, as alluded to earlier, the results obtained in the extended CRC 1 study[2] are likely due to oxygen depletion and not to a change in mechanism at higher temperatures.[16]

(2) *Validation of the use of elevated stress temperatures.* The accelerated storage of four current production, additive-free, aviation turbine fuels was conducted at three temperatures (50°, 100°, and 120° C) and at atmospheric pressure. Based on the information available, a description of the four additive-free fuels is given in Table 8. The results of the accelerated storage studies indicate the test fuels to be stable (Figures 3-5 for the 50°, 100° and 120° C temperatures, respectively; and with expanded ordinates in Figures 3A-5A). For example, at stress test conditions of 50°C/~5000 hours, which is equivalent to approximately five years at ambient

storage, only fuel #91-7, which appears to be the least stable, seems to approach the military specification maximum of 8.0 ppm hydroperoxide concentration (Fig. 3).

Because of the high storage stability of the test fuels (*i.e.*, an extremely slow rate of peroxidation), attempts to measure their classical kinetic rates of peroxidation at 50°C would likely be erroneous (Figure 3). However, in the effort to test the validity of the use of accelerated temperatures, Black and Hardy[17] adopted a pragmatic approach. The peroxidation rate of fuel #91-7 was determined based on the time taken to reach the hydroperoxide specification concentration limit of 8 ppm (MIL-T-5624). This peroxidation rate is designated, k_{8ppm}.

An Arrhenius plot of ln k_{8ppm} versus 1/T for fuel #91-7 is shown in Figure 6. The straight line obtained ($R^2 = 0.99$) further validates the use of accelerated temperatures of 100° and 120°C. Calculation of the activation energy, based on the slope of the regression line, gives a value of 23 kcal/mole, which is within the range obtained by SwRI (see SwRI studies).

B-1.3.2 Effect of air/oxygen overpressure

NRL studies on air/oxygen overpressure contributed significantly in finalizing the accelerated test conditions for predicting the storage stability of aviation turbine fuels. The test matrix comprised the following:

(1) Six JP-5 fuels of diverse origin including differences in: (a) crudes - they were obtained from different refineries/oil companies; (b) refinery processing; and (c) formulations: e.g., fuel #90-22 was derived from blending stocks; also, the use/non-use of additives including antioxidants. A brief description of the fuels is given in Table 9.

(2) Four overpressures: 15 psia (103.4 kPa), 50 psia (344.8 kPa), 100 psia (689.7 kPa) *air*, and 35 psia (241.4 kPa) *pure oxygen*. In terms of oxygen partial pressures, the three *air* overpressure values may also be expressed as 3 psia (20.7 kPa), 10 psia (69.0 kPa), and 20 psia (137.9 kPa), respectively.

(3) Four stress durations: 24, 48, 72 and 96 hours at 100°C. The 100°C stress temperature was selected (rather than 120°C) for practical reasons, which include the following: (a) a water bath could be used, should an oven not be available; (b) safety considerations - this is particularly pertinent to fuels with lower flash points; and (c) the 100°C temperature is easier to calibrate.

Table 10 ranks the test fuels in an apparent increasing order of storage stability: #90-22 being the least stable, and #91-33, the most stable fuel. The overall results indicate that the rate of hydroperoxide formation appears to be interdependent on the relative storage stability of the fuel and its stress duration, and to a lesser extent, on the air/oxygen overpressure. For example, at the same air/oxygen overpressure, hydroperoxide formation generally increased with an increase in stress duration. The extent of this increase diminished with increasing storage stability of the

fuel (e.g., #91-4). In contrast, an increase in the air/oxygen overpressure at the same test duration did not significantly increase hydroperoxide formation, except for two of the six test fuels, viz., #90-22 and #90-26, and only at stress durations greater than 48 hours. Furthermore, the significant increases in hydroperoxide formation for both #90-22 and #90-26, at 96 hour stress duration and an overpressure of 35 psia oxygen versus 100 psia air suggests that the apparent increase is attributable to the oxygen concentration rather than to the overpressure magnitude. Note, for storage-stable fuels such as #91-33, hydroperoxide formation was significantly low (<8ppm) despite increases in both the stress duration and air/oxygen overpressure. The overall scatter in the data for #91-33 likely reflects the net result of the formation and destruction of a relatively small concentration of hydroperoxides.

At a *maximum* stress duration of 48 hours, for all six fuels examined, the apparent effect of air overpressure on hydroperoxide formation does not appear to be significantly different at 50 psia versus 100 psia. Also, for stress durations of 48 hours and above, the hydroperoxide concentrations of the fuels appear to be generally lower at 15 psia air overpressure (3 psia partial pressure oxygen) than at higher levels of oxygen partial pressure.

The above results suggest the following: (a) 15 psia air may not be adequate; and (b) 50 psia air overpressure has a similar effect as 100 psia. Thus, for safety reasons, 50 psia air overpressure was selected to obviate the depletion of oxygen due to accelerated rates of peroxidation at higher temperatures. The overall results of temperature, pressure, and stress duration indicate that test conditions of 100°C at 50 psia air overpressure, for 24 hours would realistically predict storage stability at ambient conditions for approximately nine months. The pressure studies also indicate that the stress test could be extended to 48 hours (1.5 years ambient storage) should the results of the 24-hour test deem this necessary, e.g., for hydroperoxide concentration levels approaching 8 ppm. In addition, the data shown in Table 10, also focus on the potential instability of certain fuels on long term storage and hence the need for periodic assurance testing.

B-1.3.3 Use of the accelerated test method to determine the long term storage stability of worldwide fuels

NAWC and NRL used the proposed accelerated test method to determine the long term storage stabilities of a total of fourteen worldwide finished JP-5 fuels. The fuels employed were field samples and were obtained from refiners that produce JP-5 fuels for the Navy. A description of the additives' content, and the source/type of crude is given in Table 11. Of the fourteen fuels, NAWC tested nine fuels and NRL, five.

The accelerated stress conditions of 100°C at 50 psia air overpressure for 24 hours were extended to 96 hours with hydroperoxide analyses at 24 hour intervals. The results, given in Table 12, rank the fuels generally in an increasing order of storage stability. Three levels of storage stability are identified, viz., low, moderate, and high. The storage stability ranking was

based primarily on the 24-hour test period and secondarily on the 48 hour and longer stress durations. Although the results of the 24-hour test period appear to be adequate in differentiating most of the fuels, an extension to 48 hours may be useful in further differentiations. For example, after 24 hours, 12 of the 14 fuels were acceptable; after 48 hours, 9 of the 14 were acceptable; and after 72-96 hours, 8 of the 14 fuels were acceptable.

As shown in Table 12, the apparent exponential increases in hydroperoxide concentration for the low stability fuel: #90-27 at 72 and 96 hours, and for the moderate stability fuel: #90-26 at 96 hours confirm the need for periodic testing, particularly so, for fuels of marginal-poor storage stabilities (i.e., >8.0 ppm hydroperoxides). The overall results also indicate that highly storage-stable fuels appear not to deteriorate, or deteriorate extremely slowly with storage. For example, after 96 hour stress duration, which is equivalent to approximately 3 years ambient storage, all eight of the high storage stability fuels continue to meet the 8.0 ppm hydroperoxides specification with four of the eight fuels exhibiting no change in their initial low hydroperoxide content (<1.5 ppm).

The above results attest to the adequacy and sensitivity of the proposed accelerated test method for identifying fuels of differing storage stabilities and offers a reliable and practical means of predicting their long term storage stabilities. Furthermore, applicability of the test method should be considered to include all commercial turbine fuels, with and without additives, should the need arise for such determinations.

B-2.0 Part 2: Test Methodology for the Qualification of Antioxidants

B-2.1 BACKGROUND

As mentioned earlier, to ensure the storage stability of aviation turbine fuels, the military specification, MIL-T-5624M, mandated the addition of antioxidants to all JP-5 fuels and to JP-4 fuels that contain hydrogen-treated blending stocks. For these fuels, the specified concentration of antioxidant ranges from a minimum of 17.2 mg/L to a maximum of 24 mg/L fuel. For JP-4 and JP-8 fuels that do not contain hydrogen-treated blending stocks, antioxidant addition is at the option of the supplier, and is not to exceed 24 mg/L of fuel.

Historically, the twelve antioxidants permitted in the jet fuel specification (MIL-T-5624M) - all of which were hindered phenols - were developed for gum control in gasoline.[2] However, their effectiveness for peroxide control in aviation turbine fuels has never been documented. The military MIL-T-5624N specification of approved antioxidants narrowed the list to five of the previous twelve. This selection was based on limited evaluations conducted at NAWC.[19,20] Consequently, in an effort to substantiate the decision for selecting only five of the original 12 approved antioxidants, the effectiveness of 13 of the 14 antioxidants listed in MIL-T5624L was evaluated by SwRI and NIPER in two fuels at several accelerated stress temperatures/times. These evaluations have been reported in/as Final Reports,[8,12] consequently, only pertinent details will be highlighted. In addition, an overall evaluation of the test results is presented, the objective of which was to develop a test methodology for the future qualification of antioxidants for MIL-T-5624 specification.

B-2.2 EXPERIMENTAL

Antioxidants Screened: A list of the thirteen antioxidants screened by SwRI and Niper are listed in Table 13A. Table 13B details the formulations of antioxidants F, G, H, and J as prepared by NIPER. In all cases, the additive concentration level employed was at the lower specification limit, viz., 17 mg/L.

Pressure Reactors/Stress Conditions: The pressure reactors used by SwRI and NIPER to screen the antioxidants are described in Table 4. For these screenings, both pressure reactors were operated at 35 psia (240 kPa) oxygen overpressure. The stress temperatures employed at SwRI were 100° and 120°C and at NIPER, 65° and 100° C.

Test Fuels: The two fuels used to screen the antioxidants were not finished jet fuels but blending stocks used in jet fuels. These are #18496 and #18497 - also described as Fuels A and B, respectively, in NIPER's report.[8] A brief compositional/properties description of both fuels, taken from NIPER's report,[8] follow:

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Fuel 18496 was a 100%- hydrocracked blending stock from a West Coast refinery and was intended to represent a relatively unstable fuel. This stream alone could not be used as a JP-5 fuel for the following reasons: it exceeded the specification limits for aromatics (41.6% vs 25% max), distillation end point (317°C vs 300°C max), and freeze point (-10.3°C vs -46°C); and was below the limits for flash point (46°C vs 60°C min), aniline gravity product (3867 vs 4500 min), hydrogen content (12.7 wt% vs 13.4 wt% min) and smoke point (14.3 mm vs 19 mm).

Fuel 18497 was a blend of 76 percent hydrocracked stock and 24 percent hydrotreated light cycle oil from a Texas refinery with a mixed crude slate. This fuel met most of the specification limits except for a slightly low flash point (56°C vs 60°C).

B-2.3.0 RESULTS AND DISCUSSION
B-2.3.1 General

SwRI evaluated the effectiveness of the antioxidants screened, based on their induction periods. The induction period of each antioxidant was determined from the intercept of the regression lines for its induction and post induction periods.[12] Thus, the actual induction period value is derived indirectly and may or may not be exact. NIPER evaluated antioxidant effectiveness based on the time taken for the hydroperoxide levels to reach 100 ppm.[8] Such a criterion appears rigorous but does not relate to the military specification of 8.0 ppm. In a separate study, a serial dilution method was investigated for evaluating the effectiveness of antioxidants. This method involves serial dilutions of the antioxidant and compares effectiveness based on concentration.[18] In this report, a more pragmatic approach was taken and is as described below:

The effectiveness of the 13 antioxidants screened was evaluated on the basis of their performance at specific stress test conditions. The stress conditions selected were based on the availability of complete sets of data. In addition, an effort was made to include stress tests *that showed differentiation in antioxidant efficacy* both at the low and high levels of hydroperoxides of the non-doped fuel. Two criteria were adopted to evaluate relative antioxidant efficacy in the two fuels examined by both SwRI and NIPER. These criteria are based on the following:

(a) *Overall Effectiveness.* This is based on the capability of the antioxidant to control hydroperoxide formation to the specification limit of 8.0 ppm in the stress tests selected, for both fuels. Thus, for the same stress test and fuel, those antioxidants that controlled hydroperoxide levels to 8.0 ppm or lower were categorized as having passed. Those that controlled hydroperoxide levels within the range 8.1 to 10.0 ppm were categorized as marginal. And, those that effected hydroperoxide levels of 10.1 ppm and above were categorized as having failed. However, for the purpose of ranking (see (b) below), antioxidant overall effectiveness was more rigorously categorized as pass or fail, where 'marginal' is included as a 'fail'.

(b) *Overall Ranking*. This is based primarily on the antioxidant overall effectiveness and secondarily on its average ranking for the specific stress temperatures/times selected for both fuels.

The results (Tables 14-15: A-C, and Table 16) suggest that the effectiveness of the 13 antioxidants screened varied with the fuel, the antioxidant structure, and the stress test conditions. These factors are subsequently discussed.

B-2.3.2 Fuel effect

In fuel 18496, which was selected as representing a poor storage stability fuel (*see* Experimental B-2.2), antioxidant A ranked at the top for both criteria and exhibited no failures for the stress tests examined (Table 14C). In fuel 18487, however, antioxidant B ranked at the top and exhibited no failures, whilst antioxidant A ranked seventh and included two failures out of six screenings (Table 15C).

Based on the stress tests examined and the imposed criteria, the seven top ranking antioxidants in fuel 18496 were: A > > H > B > E > F > > C > G (Table 14C). And in fuel 18497, the seven top rankings were: B > H > E > F > C > D > A (Table 15C). For both fuels, the seven overall top ranking antioxidants were: B > H > E > F > A > C > D (Table 16). Although their orders of ranking varied, SwRI and NIPER also ranked these antioxidants in the top seven. Differences in the ranking order may be related to the different criteria adopted. Furthermore, these seven antioxidants include the five antioxidants currently approved in specification MIL-T-5624N as well as two others. H, a top ranking antioxidant, and F were excluded from the MIL-T-5624N specification because they contained smaller percentages of the component(s) known to be effective[20] and because of possible problems in validating their formulation packages. Nevertheless, the high ranking order of H, in particular, warrants further investigation of its cost effectiveness and reliable formulation packaging. Of the other antioxidants screened, G appears marginal, whereas, M, L, I, N, and J performed consistently poorly in both fuels relative to the other antioxidants in most of the stress tests performed.

B-2.3.3 Antioxidant structural effect

The improved performance of antioxidants such as: A and B (single components), E and F (mixtures that contain 72 and 55 percent, respectively of B), and H (mixture of 35 percent A, approximately 22 percent of B and other hindered phenols - see Table 13B) are consistent with Scott's findings[13b] regarding the effect of antioxidant structure on its efficacy. The lower efficacy of antioxidants M and I are likewise explained. For convenience, Scott's findings[13b] are highlighted below:

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1.   Electron releasing groups in the *ortho* and *para* positions markedly increase antioxidant activity.

2.   *Alpha* branched *ortho* alkyl groups considerably increase antioxidant activity whereas such group substitutions in the *para* position decrease it.

3.   For petroleum, the combination of two *ortho tertiary* alkyl groups are not as effective as one methyl and one tertiary butyl.

Such structural effects appear to explain the differences in effectiveness amongst the antioxidants examined. For example:

(a) the overall top ranking efficacy of B: this antioxidant exhibits all the structural advantages reported *(findings 1-3)*;

(b) the high rankings of E and F: both antioxidant formulations contain high percentages of B; also the higher ranking of antioxidant E versus F is likely a concentration effect: E contains 17 percent more of B, than F;

(c) the high efficacy of A *(findings 1 and 2)*, but lower than that of B *(finding 3)*;

(d) the improved performance of H versus A suggests a possible synergistic effect of its components, which includes 36% A and 22% B, as well as other components (*see* Table 13 B);

(e) the efficacies of C, and D (D contains 75 percent C) are lower than that of B *(finding 3)* and A *(finding 1)*, but higher than that of M and I *(finding 2)*.

(f) the poor performance of J: as shown in Table 13B, none of its components exhibit the findings for increased antioxidant activity, particularly, findings 2 and 3.

B-2.3.4 Stress test effect

As shown in Tables 14C and 15C for fuels 18496 and 18497, respectively, the antioxidants' rankings at 65°, 100°, and 120°C show some similarities, as well as, noted exceptions. For example, as was mentioned earlier, for the various stress tests in both fuels, antioxidants: B, H, E, F, A, C, and D generally ranked in the top seven whereas: L, I, N, and J ranked in the lowest four. Noted exceptions include antioxidant B, which ranked 8th in fuel 18496 at 100°C/15 hr (Table 14C) and antioxidant C, which ranked 8th at 120°C/12 hr in fuel 18497 (Table 15C). The overall differences in ranking, in the different stress tests, for the same fuel, are attributable to the stress temperature/duration.

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Categorizations of the antioxidants into: pass, marginal, or fail, are also stress duration dependent. For example, for fuel 18496/100°C (Table 14 B), at 10 hr stress duration, all the antioxidants except "I" appear to pass the specification limit. At 15 hr stress duration, a greater differentiation in efficacy is observed: only six of the 13 antioxidants passed. However, at 25 hr, only one (A) passed the SwRI stress test, and none passed the Niper test. Note, the poor differentiation at stress duration of 25 hour/100°C is possibly related to fuel 18496 being inherently poor (*see* Experimental B-2.0) in conjunction with the high concentration level of oxygen (35 psia oxygen overpressure) used in the stress tests. Similar differences in categorization of the antioxidants - due to the severity of the stress tests were also observed for fuel 18497. These results also point to the importance of selecting adequate stress conditions for qualifying antioxidants.

B-2.3.5 Recommendations for future qualification of antioxidants

(1) *Test Method*: The accelerated test conditions of 100°C stress temperature and 50 psia air overpressure that have been proposed for predicting the storage stability of aviation fuels (*see* Part 1) should be adopted for qualifying antioxidants. However, a minimum of three stress periods, 24, 48, and 96 hours should be used for evaluating antioxidants for qualification purposes. These stress periods afford better differentiation of the variability in fuels and antioxidant efficacy. The excellent differentiation in storage stabilities obtained for the 14 finished JP-5 worldwide fuels, when evaluated using this method (*see* section A-3.3), supports its adoption. Furthermore, a 96-hour stress period has the added advantage of extending the predictability to 3 years at ambient storage.

(2) *Fuels*: The test fuels should include current production fuels that exhibit poor, marginal, and good storage stabilities, on a long term basis. Such fuels are best defined by the relative lengths of their induction periods. Thus, the induction period of a good fuel should be significantly greater than that of a poor fuel by a factor of at least two. And, the induction period of a marginal fuel would be of intermediate length between a good and poor fuel. However, for the purpose of qualifying antioxidants, because the military specification limit for hydroperoxide concentration is 8.0 ppm, poor, marginal, and good fuels are best identified based on the relative times taken for the fuel to exhibit a hydroperoxide concentration level within 8-16 ppm. This stress time is defined as, $t_{8-16ppm}$.

In the definition of $t_{8-16ppm}$, narrowing the limits of the hydroperoxide concentration level to 8-16 ppm, affords a rigorous means of differentiating fuels of diverse stabilities. This is particularly important in the selection of the test fuels. Thus, for a poor fuel, $t_{8-16ppm}$ would be 24 hours; for a marginal fuel, $t_{8-16ppm}$ would be 48 hours; and, for a good fuel, $t_{8-16ppm}$ would be 96 hours and greater. Although high storage stability fuels may not need an antioxidant, it is necessary to ensure that the selected antioxidants exhibit no adverse effects in such fuels, hence the need for their inclusion in the test matrix.

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(3) *Antioxidants*: The test protocol should be validated using good, marginal, and poor antioxidants, which are arbitrarily defined as follows: At stress conditions of 100°C, 50 psia air overpressure and stress periods of 24, 48, 72, and 96 hours, a good antioxidant may be defined as one for which the hydroperoxide concentration is kept within a level < 8.0 ppm at 24-96 hours stress periods; a marginal antioxidant, one for which the hydroperoxide concentration is within 8-10 ppm at 48 hour stress period; and a poor antioxidant, one for which the hydroperoxide concentration is > 10 ppm at 24 hour stress period. These criteria also further serve to characterize antioxidants on a more rigorous pass/fail basis. Thus, good antioxidants are characterized as 'passes', whereas marginal and poor antioxidants, as 'fails'.

(4) *Test Criteria*: Antioxidants should be evaluated on the rigorous pass/fail basis described above. The relative performance of the antioxidants should be further evaluated using two references, viz., the corresponding neat fuel (no additive present) and the most effective antioxidant. Selections should be based on: (a) antioxidants that control the hydroperoxide concentration to a level of 8.0 ppm max., for the longest test duration period, relative to the corresponding neat fuels of good, marginal, and poor storage stabilities; and (b) antioxidants that are similar to, or are approximately 80% as effective as the most effective candidate.

Pressure Reactors. NAWC has recommended NRL's LPR for conducting accelerated stress tests.[21] This recommendation is based on their evaluation of the three pressure reactors described in Table 4. The LPR was found[21] to provide a more controlled environment than the previous bottle tests - an important factor for the effective analysis of reaction rates. Also, the LPR is more cost effective than the reactor used at SwRI.

C-1 CONCLUSIONS

Rapid and practical methodologies were developed for reliably predicting the long term storage stabilities of aviation turbine fuels and for the evaluation of antioxidant effectiveness for qualification purposes. The method is based on the collective results of extensive rigorous studies performed by the four participating laboratories, viz., Southwest Research Institute (SwRI), San Antonio, Texas; the Naval Research Laboratory (NRL) Washington, D.C.; the Naval Air Warfare Center (NAWC),Trenton, New Jersey; and the National Institute of Petroleum and Energy Research (NIPER), Bartlesville, Oklahoma.

The proposed accelerated method for predicting the long term storage stabilities of aviation turbine fuels entails conducting the stress test in a Low Pressure Reactor at 100°C stress temperature, and 50 psia (344.8 kPa) overpressure air for 24 hours with the option to extend to 48 hours if deemed necessary. The 100°C stress temperature has been validated to be predictive of long term storage at ambient conditions. The use of 50 psia air overpressure appears to be ample in preventing oxygen depletion at this elevated temperature. The reactor of choice was the Low Pressure Reactor (LPR), which was designed by the Naval Research Laboratory and is commercially available from a number of vendors. Use of the method to determine the long term

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storage stabilities of worldwide current production fuels indicate the 24-48 hour stress duration to be adequate in differentiating fuels with differing stabilities. Studies that extended the stress test duration to 96 hours confirm the Navy's current protocol for periodic testing on a six monthly basis.

Recommendations for a test methodology to evaluate the effectiveness of antioxidants for future qualification in MIL-T-5624 specification include the following:

1. Adopt the proposed accelerated stress test conditions of 100°C temperature and 50 psia air overpressure. And, for better differentiation of antioxidant effectiveness in the test fuels examined, use a minimum of three stress periods, viz., 24, 48 and 96 hours.

2. Use fuels of poor, marginal, and good storage stabilities, as defined in this paper.

3. Screen antioxidants of good, marginal and poor effectiveness, as defined in this paper.

4. Evaluate the effectiveness of the antioxidant based on its ability not to exceed the hydroperoxide concentration specification limit of 8.0 ppm max. To determine the relative performance of promising antioxidants, two references are recommended, viz., the corresponding non-doped fuel and the most effective candidate, as defined in this paper.

ACKNOWLEDGMENTS

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Table 1. Some Experimental Details of the Early Test Programs

Test Program	No. of Fuels	No. of Labs	Procedure			
			Sample[a] (mL)	Bottle[b] (mL)	Stress Test	
					Temp (°C)	Duration (dy)
Initial	19	1 (NRL)	250: x2; x3	500	100	30
CRC 1: 1982	7	6	350: x2	500	100	7
	4 (of above 7)	1 (NRL)	350: x2	500	43	210
					65	70
					80	28
CRC 2: 1984	5: Aerated[c]	6	400: x2	500	65	56
CRC 3: 1986	9: Aerated[c]	8	400: x3	500 LC[d]	65	42

[a] Multiplicity of sample testing: x2, in duplicate; x3, in triplicate.

[b] Bottles were *capped* unless otherwise indicated.

[c] Fuels saturated with air prior to testing and at sampling time, caps left off for 15-30 mins.

[d] LC: loosely capped.

Table 2. Fuels Used in the Early Test Programs

Test	Fuels No. and Type	origin[a]/ treatment[b]	Antioxidant[c]: # doped fuels
Initial:	1 Jet A	HT	+
	9 current production JP-5s		+: all
	5 Shale II JP-5s	shale	+: two
	4 Shale II DFMs	shale	+: two
CRC 1:	JP-5	severe HT	+ and -
	JP-5: straight run	mild HT	+ and -
	JP-4		-
	Jet A	moderate HT	-
	JP-5	oil shale	-
CRC 2	JP-5	severe HT	+ and -
	JP-4	shale/severe HT	+
	JP-4		+
	JP-5	moderate HT	+
CRC 3	Jet A	mild HT	-
	Blending stock	moderate HP	-
	Blending stock	severe HP	-
	Blending stock	HT	-
	JP-4	shale/HT	-
	Jet A: blending stock	HF	-
	Jet A: blending stock	HC	-
	JP-5	no HT	-
	JP-5	moderate HT	-

[a] petroleum derived, unless otherwise stated.
[b] HT: hydrotreated; HP: hydroprocessed; HF: hydrofined; HC: hydrocracked.
[c] +: added; -: not added.

Table 3. Experimental Matrix Employed in Verifying the Use of Accelerated Temperatures

Lab	Fuel No.	Oxygen Pressures Employed in kPa, at Stress Temperature (°C)/Stress Period Specified[a]					
		43°/ 24wk[b]	50°/ 60.8wk	65°/ 6wk[b]	80°/ 70 hr	100°/ 25hr	120°/ 6 hr
SwRI	0464	21	-	-	790, 1140	240, 790	240
	11310	21	-	-	790, 1140	240, 790	240
	11310A	21	-	-	790, 1140	240, 790	240
	11381	21	-	-	790, 1140	240, 790	240
	AV-284	-	-	21	-	240/55hr	240/15hr
	AV-285	-	-	21	-	240/55hr	240/15hr
	15708	21/50wk	-	-	240	240	240/25hr
	16581	21/50wk	-	-	240/90hr	240/50hr	240/25 hr
	18496	-	-	-	240/215hr	240[c]/50hr	240[c]/8hr
	18497	-	-	-	240/185hr	240[c]/55hr	240[c]/8hr
NRL[d]	#91-7	-	21/ 28.6wk	-	-	21/48hr	21/72hr
	#91-5	-	21	-	-	21/77hr	21/30hr
	#91-4	-	21	-	-	21/144hr	21/48hr
	#91-1	-	21	-	-	21/72hr	21/120hr

[a] Unless otherwise indicated.
[b] Bottle storage tests at atmospheric pressure.
[c] In addition to the neat fuel, antioxidant studies involving 13 antioxidants also performed (Part 2).
[d] 100 mL fuel in 500 mL Kimax flasks at atmospheric pressure.

Table 4. Reactor Design Differences

Reactor	Features	Advantages	Disadvantages
SwRI	316 stainless steel, 600 mL capacity pressurized vessel (modified PARR mini reactor, No. 4573); sample (300 mL); stirred magnetically and heated via an external electrical heating element.	Allows sample introduction and withdrawal to and from the liquid/vapor phase without need for de-pressurizing the reactor. No cross-contamination	Costly, and only one sample can be tested at a time.
NRL	pressurized vessel; 22 (125 mL) bottle capacity; sample:100 mL/bottle; oven used for heating.	Less costly than SwRI's. Multiple samples tested at a time.	Samples removed only at completion of test. Possibility of sample cross-contamination
NIPER	Aluminum pressure cooker* 14 (100 mL) bottle capacity; Sample: 75 mL/bottle; oven used for heating.	Less costly than SwRI's. Multiple samples tested at a time.	Samples removed only at completion of test. Possibility of sample cross-contamination.

* Adapted for safe operation

Table 5. Description of the Fuels SwRI Used

Fuel No.	Description*
0464	Jet A, straight run, additive-free, salt dried, clay-treated
11310A	Hydrocracked, alumina treated**
11381	Hydrocracked
11381A	Fuel #11381, alumina-treated**
AV-284	Hydrofined
AV-285	Hydrocracked
15708	Hydroprocessed
16581	Hydroprocessed
18496	Hydrocracked
18497	Mixture of 76% hydrocracked + 24% hydrotreated light gas oil

* According to the source refineries, all test fuels were free of added antioxidants.
** Alumina treatment removes existent peroxides and other polar compounds.

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Table 6. Activation Energies and R^2 Values Based on Linear Regression Analysis of the Arrhenius Plots (ln k = ln A - E_a/RT)

Fuel No.	Period	Temperature Range, °C	E_a, kcal/mole	R^2
0464	Full Range	43-120	19.42	0.968
11310A*	Full Range	43-120	21.16	0.996
11381	Full Range	43-120	30.28	0.982
11381A*	Full Range	43-120	22.04	0.998
AV-284	Induction Period	65-120	27.04	0.989
	Post Induction Period	65-120	20.45	1.00
AV-285	Induction Period	65-120	27.08	0.999
	Post Induction Period	65-120	20.66	1.00
15708	Induction Period	43-120	28.37	0.990
	Post Induction Period	43-120	23.33	0.998
16581	Induction Period	43-120	23.65	0.988
	Post Induction Period	43-120	23.03	0.990
18496	Induction Period	80-120	28.49	1.00
	Post Induction Period	80-120	22.73	0.999
18497	Induction Period	80-120	26.82	0.998
	Post Induction Period	80-120	24.98	0.996

* Alumina pre-treated

Table 7. Effect of Capped *vs* Vented Bottle Tests on Fuel Peroxidation
(Accelerated Storage Conditions: 65 °C/atmospheric pressure/12 weeks)

Fuel #: description	Hydroperoxide concentration after 12 wks (ppm)	
	Capped	*Vented*
#90-4: JP-5 hydrocracked blending stock; additive free	74.0	5508*
#87-83: Jet A	61.4	3347 (4020 ppm after 10wks)
#90-3: JP-5 blending stock: 76% hydro-cracked + 24% hydrotreated light gas oil; additive free	104.5	2778*
Shale II: finished JP-5	17.7	28*
n-Dodecane: silica gel treated**	103.7	92*

*   Linear peroxidation.
** Pre-treated with silica gel (250 g of 100-200 mesh activated silica gel added to 2 L dodecane, and the mixture stirred magnetically) to remove polar species that may affect the hydro-peroxide formation rates.

Table 8. Current Production Fuels Used in the Accelerated Stress Temperature Studies at NRL

Fuel No.	Type	Description
#91-7	JP-5 without additives	Contained no additives. This fuel was produced by hydrotreatment of straight run kerosene distilled from a refinery slate consisting of 76% sour Arabian crudes and 24% mixed sweet domestic crudes.
#91-5	Jet A-1	Super K hydrotreated kerosene. Was found to exhibit high thermal stability.
#91-4	JP-5	additive free
#91-1	JP-5	additive free

Table 9. JP-5 Fuels Used in the Overpressure Studies at NRL

Fuel No.	Description
#90-22	Blending stock doped with 22.6 mg/L 2,6-di-tert butyl 4-methyl phenol
#90-26	DF*: hydrocracked, hydrotreated; additives: anti-icing inhibitor + antioxidant + corrosion inhibitor
#91-7	JP-5 without additives (also, *see* Table 8)
#90-23	DF*: hydrofined (1400 psig); additives: antioxidant + corrosion inhibitor
#91-4	additive free
#91-33	hydrotreated; additive free

* Diagnostic fuel: additional information on these fuels is given in Table 11.

Table 10. Effect of Air/Oxygen Overpressures on Fuel Peroxidation at 100°C with Time

Fuel No.	Stress Time* (hr)	Equiv. Storage Time (approx.)	Hydroperoxide Concentration in ppm at Specified Pressures: air/oxygen			
			Partial Pressures, Air			Pure Oxygen
			15 psia	50 psia	100 psia	35 psia
#90-22	24	9 mth	1.27	2.91	4.02	4.20
	48	1.5 yr	4.44	10.02	10.67	14.76
	72	2.2 yr	10.88	28.93	44.97	76.41
	96	3 yr	23.55	204.81	575.01	1387.8
#91-7	24	9 mth	2.34	5.13	5.39	4.27
	48	1.5 yr	8.35	12.47	14.91	11.23
	72	2.2 yr	20.14	19.72	24.28	21.50
	96	3 yr	30.89	34.34	36.38	41.47
#90-23	24	9 mth	4.96	4.95	5.71	5.84
	48	1.5 yr	9.11	11.64	13.32	14.62
	72	2.2 yr	18.28	19.52	22.58	21.20
	96	3 yr	27.79	30.29	38.66	37.35
#90-26	24	9 mth	1.18	1.41	1.85	2.24
	48	1.5 yr	3.81	4.28	5.21	8.26
	72	2.2 yr	5.10	8.51	16.90	18.96
	96	3 yr	10.33	16.35	47.97	220.0
#91-4	24	9 mth	0.66	1.78	1.75	2.65
	48	1.5 yr	3.71	4.17	6.38	5.69
	72	2.2 yr	5.40	6.69	8.06	8.04
	96	3 yr	7.68	7.99	11.06	10.80
#91-33	24	9 mth	1.49	1.33	3.19	2.20
	48	1.5 yr	0.83	0.92	3.17	2.34
	72	2.2 yr	2.38	0.53	3.18	1.84
	96	3 yr	1.84	0.70	2.87	1.80

* At time zero, the hydroperoxide concentration was below the level of detection in all cases.

Table 11. Description of the Worldwide Finished JP-5 Fuels

Fuel No.	Additives[a]	Source/Type of Crude and Treatment[b]
#90-24	AO: Du Pont AO-37; CI: IPC 4445	Alaskan North slope (85%) + San Joaquin Valley (15%); HF
#90-27	FSII: 0.18%v DIEGME AO: AITEC 4733 CI: NALCO 5403	Kuwait Export HC; HT
#90-14	FSII: 0.18%v DIEGME AO: STIA 26/24 CI: NALCO 5403	Saudi Arabian (Light)/Algerian Mild HT
#90-23	same as #90-24	same as #90-24
#90-7	AO: IPC 4650 CI: IPC 4445	Alaskan North slope; NGL Injection, secondary and tertiary recovery[c]; HC; SD, and hydrodesulfurization
#90-26	same as #90-27	same as #90-27
#90-5	FSII:0.15-0.2%v DIEGME AO: Nalco 5275 CI: Nalco 5403	West Texas Intermediate; sweet: 0.2-0.4 wt% sulfur; SD and Merox treatment.
#90-13	same as #90-14	same as #90-14
#90-16	AO: Ethyl 733 (80% active)	West Texas Sour 41% + Prudhoe Bay 43% + South Texas Mix 13% + Cano Limon 3%; SD; mild HT.
#90-6	same as #90-5	same as #90-5
#90-12	FSII: 0.16%v methacarbatol; AO: Ethyl 733 CI: DC14A	Venezuelan Furrial, Colombian Cano Limon, and Mexican Olmeca; caustic wash.
#90-11	same as #90-12	Venezuelan Lagomedio, Mesa Ecuadorian Oriente, Alaskan North slope.
#90-9	AO: name not given	Hawkins/Cabinda/South Louisiana; SD
#90-8	same as #90-9	same as #90-9

[a] AO: antioxidant; CI, corrosion inhibitor; FSII: fuel system icing inhibitor.
[b] Refinery Process Techniques: HC, hydrocracking; HF, hydrofined; HT, hydrotreatment; SD, straight distillation.
[c] Crude production techniques used other than normal pumping or natural pressure.

Table 12. Application of the Accelerated Test Method to the Worldwide Finished JP-5 Fuels
Test Conditions: 100 °C/50psia air overpressure at stress periods shown

Storage stability: fuel ID#	Hydroperoxide Concn in ppm at stress periods:			
	24 hrs	48 hrs	72 hrs	96 hrs
Low stability: #90-24*	15.1	23.7	42.4	40.6
#90-27*	8.1	29.2	523.0	1437.2
Moderate stability: #90-14*	7.2	15.5	39.3	33.6
#90-23**	4.8	10.0	17.9	28.9
#90-7**	4.0	8.0	11.3	14.6
#90-26**	1.8	4.3	16.6	241.3
High Stability: #90-5*	3.6	2.3	4.4	5.3
#90-13**	2.1	5.0	3.1	6.4
#90-16**	2.7	3.8	4.8	5.0
#90-6*	1.9	2.7	7.4	4.2
#90-12*	1.5	1.3	1.0	0.9
#90-11*	1.4	1.0	1.3	1.0
#90-9*	0.7	0.3	1.8	0.9
#90-8*	0.4	0.9	0.5	0.6

* Accelerated storage stability test performed by NAWC.
** Accelerated storage stability test performed by NRL

Table 13A. Formulations of the Thirteen Antioxidants Screened
MIL-T-5624 (L)*

A. 2,6-di-tert-butyl-4-methylphenol

B. 6-tert-butyl-2,4-dimethylphenol

C. 2,6-di-tert-butylphenol

D. 75 percent min 2,6-di-tert-butylphenol (C)
    25 percent max tert-butylphenols and tri-tert-butylphenols

E. 72 percent min 6-tert-butyl-2,4-dimethylphenol (B)
    28 percent max tert-butyl-methylphenols and tert-butyl-dimethylphenols

F.** 55 percent min 6-tert-butyl-2,4-dimethylphenol (B)
    45 percent max mixture of tert-butylphenols and di-tert-butylphenols

G.** 60 to 80 percent 2,6-dialkylphenols
    20 to 40 percent mixture of 2,3,6-trialkylphenols and 2,4,6-trialkylphenols

H.** 35 percent min 2,6-di-tert-butyl-4-methylphenol (A)
    65 percent max mixture of methyl, ethyl, and dimethyl-tert-butylphenols

I. 60 percent min 2,4-di-tert-butylphenol
    40 percent max mixture of tert-butylphenols

J.** 30 percent min mixture of 2,3,6-trimethylphenol and 2,4,6-trimethylphenol
    70 percent max mixture of dimethylphenols

L. 55 percent min butylated ethyl phenols
    45 percent max butylated methyl and dimethyl phenols

M. 45 percent min 4,6-di-tert-butyl-2-methylphenol
    40 percent min mixture of 6-tert-butyl-2-methylphenol and 2,4,6-tri-tert-butylphenol
    15 percent max mixture of other butylated phenols

N. 75 percent min mixture of di- and tri-isopropylphenols
    25 percent max mixture of di- and tri-tert-butylphenols

* Thirteen of the fourteen antioxidants listed in MIL-T-5624L were screened. Antioxidant K was dropped from the test matrix. In the subsequent military specification, MIL-T-5624M, antioxidant N was dropped. Thus,the 12 antioxidants in MIL-T-5624M are as follows: antioxidants, A-J, listed above are similarly identified, but antioxidants L and M, in 5624L became K and L, respectively, in 5624M.

** See Table 13B for a more detailed analysis.

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Table 13B. Formulations* of Antioxidants: F, G, H and J Used in Evaluations

F. 56% 6-tert-butyl-2,4-dimethylphenol (B)
    22% 2,6-di-tert-butylphenol (C)
    22% 4-tert-butylphenol

G. 20% 2,3,6-trimethylphenol
    20% 2,4,6-trimethylphenol
    60% 2,6-di-tert-butylphenol (C)

H. 36% 2,6-di-tert-butyl-4-methylphenol (A)
    21% 2-tert-butyl-6-methylphenol *(finding 2)*
    21% 2-tert-butyl-4-methylphenol *(finding 2)*
    22% 6-tert-butyl-2,4-dimethylphenol (B)

J. 15% 2,3,6-trimethylphenol
    15% 2,4,6-trimethylphenol
    14% 3,5-dimethylphenol
    14% 2,5-dimethylphenol
    28% 2,4-dimethylphenol
    14% 2,6-dimethylphenol

* Prepared by NIPER

Table 14A
Antioxidants Screened by SwRI and NIPER at Temperatures/Durations Indicated and at 240 kPa (35 psia) Oxygen
In Fuel 18496 at 17 mg/L

hydroperoxide concentration, ppm

65°C/672 hr (28 dy)			65°C/960 hr (40 dy)			120°C/3 hr			120°C/6 hr		
AO	NIPER	CLASS*	AO	NIPER	CLASS*	AO	SwRI	CLASS*	AO	SwRI	CLASS*
A	6.7	pass	A	9.2	margn	B	4.4	pass	A	20.3	fail
H	6.8	pass	H	12.2	fail	A	5.3	pass	B	47.6	fail
B	7.7	pass	B	14.5	fail	F	6.3	pass	H	57.8	fail
F	8.5	margn	E	18.4	fail	E	7.3	pass	E	62.4	fail
E	9.0	margn	F	20.3	fail	C	9.0	margn	F	68.9	fail
D	12.0	fail	C	22.5	fail	H	10.2	fail	C	102	fail
C	12.1	fail	D	25.3	fail	G	10.9	fail	D	119	fail
G	12.6	fail	G	33.9	fail	D	10.9	fail	G	132	fail
M	14.4	fail	M	37.8	fail	L	18.5	fail	L	372	fail
I	17.4	fail	N	63.8	fail	M	19.4	fail	N	372	fail
N	19.1	fail	I	110	fail	N	21.2	fail	M	380	fail
L	19.9	fail	L	112	fail	J	27.0	fail	J	488	fail
J	29.4	fail	J	185	fail	I	28.1	fail	I	745	fail
NONE	453	fail	NONE	453**	fail	NONE	32.5	fail	NONE	1384	fail

* Classification of the fuels with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

** For 28 dys/65°C. Peroxidation data for longer stress duration not available for the neat fuel.

Table 14B
Antioxidants Screened by SwRl and NIPER at 100°C/240 kPa (35 psia) Oxygen for Durations Indicated
In Fuel 18496 at 17 mg/L

hydroperoxide concentration, ppm

10 hr			15 hr			25 hr			25 hr		
AO	SwRl	CLASS*	AO	SwRl	CLASS*	AO	SwRl	CLASS*	AO	NIPER	CLASS*
H	2.3	pass	A	2.6	pass	A	4.8	pass	A	11.0	fail
A	2.6	pass	H	6.3	pass	H	9.6	margn	B	11.8	fail
E	3.6	pass	G	6.3	pass	E	14.4	fail	E	12.5	fail
J	4.8	pass	F	6.8	pass	B	16.0	fail	H	13.0	fail
C	4.8	pass	E	6.8	pass	F	17.6	fail	F	15.4	fail
F	4.8	pass	C	7.3	pass	C	18.5	fail	G	21.5	fail
B	5.8	pass	D	9.6	margn	D	21.2	fail	M	21.8	fail
D	5.8	pass	B	9.6	margn	G	25.0	fail	D	22.2	fail
L	5.8	pass	M	10.9	fail	M	32.5	fail	C	22.2	fail
N	6.8	pass	L	11.6	fail	N	38.4	fail	L	22.9	fail
M	7.3	pass	I	12.3	fail	L	59.3	fail	N	23.6	fail
G	7.8	pass	N	13.0	fail	I	65.6	fail	J	26.1	fail
I	10.2	fail	J	13.0	fail	J	65.6	fail	I	34.3	fail
NONE	10.9	fail	NONE	27.0	fail	NONE	346	fail	NONE	491	fail

* Classification of the fuels with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

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Table 14C
Ranking and Classification of Antioxidants Screened at Three Stress Temperatures/Durations Indicated and at 240 kPa (35 psia) Oxygen
Based on Stress Tests Performed at NIPER and SwRI
In Fuel 18496 at 17 mg/L

AO	65°C NIPER	100°C SwRI		100°C NIPER	120°C SwRI		Rank[b]	Classification		
	28 dy[a]	15 hr[a]	25 hr	25 hr	3 hr[a]	6 hr		Pass	Margn	Fail
A	1 pass	1 pass	1	1	2 pass	1	1	3	0	0
H	2 pass	2 pass	2	4	6 fail	3	2	2	0	1
B	3 pass	8 margn	4	2	1 pass	2	3	2	1	0
E	5 margn	5 pass	3	3	4 pass	4	4	2	1	0
F	4 margn	4 pass	5	5	3 pass	5	5	2	1	0
C	7 fail	6 pass	6	9	5 margn	6	6	1	1	1
G	8 fail	3 pass	8	6	7 fail	8	7	1	0	2
D	6 fail	7 margn	7	8	8 fail	7	8	0	1	2
M	9 fail	9 fail	9	7	10 fail	11	9	0	0	3
L	12 fail	10 fail	11	10	9 fail	9	10	0	0	3
N	11 fail	12 fail	10	11	11 fail	10	11	0	0	3
I	10 fail	11 fail	12	13	13 fail	13	12	0	0	3
J	13 fail	13 fail	13	12	12 fail	12	13	0	0	3
NONE[c]	453 ppm	27 ppm			32.5 ppm					

[a] For these stress conditions, the fuels are classified with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

[b] Based on the antioxidant's overall effectiveness as described on p.14, in conjunction with its average ranking.

[c] Hydroperoxide concentration of the neat fuel at stress conditions specified.

Table 15A
Antioxidants Screened by SwRI and NIPER at Temperatures/Durations Indicated and at 240 kPa (35 psia) Oxygen
In Fuel 18497 at 17 mg/L

	hydroperoxide concentration, ppm							
	65 °C/3864 hr (161 dy)			120 °C/8 hr			120 °C/12 hr	
AO	NIPER	CLASS[a]	AO	SwRI	CLASS[a]	AO	SwRI	CLASS[a]
H	1.3	pass	F	2.0	pass	B	5.3	pass
B	1.3	pass	H	2.3	pass	F	5.8	pass
E	1.5	pass	A	2.9	pass	H	7.3	pass
F	1.7	pass	B	2.9	pass	E	9.0	margn
C	1.8	pass	E	4.8	pass	A	13.0	fail
A	1.8	pass	D	5.8	pass	G	15.2	fail
D	2.0	pass	C	6.3	pass	D	16.0	fail
G	15.7	fail	G	7.3	pass	C	20.3	fail
M	30.1	fail	L	12.3	fail	M	44.9	fail
L	63.1	fail	M	13.7	fail	L	56.3	fail
J	124[b]	fail	N	16.8	fail	N	139	fail
I	182[c]	fail	I	25.0	fail	I	328	fail
N	192[d]	fail	J	38.4	fail	J	428	fail
NONE	103[e]	fail	NONE	2905	fail	NONE	2905[f]	fail

[a] Classification of the fuels with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

[b] 3336 hr (139 dy); [c] 3192 hr (133 dy); [d] 3552 hr (148 dy); [e] at 65 °C/1560 hr (65 dy): peroxidation data for longer stress period not available;

[f] at 120°C/8 hr: peroxidation data for longer stress duration not available.

Table 15B
Antioxidants Screened by SwRI and NIPER at 100°C/240 kPa (35 psia) Oxygen for Durations Indicated
In Fuel 18497 at 17 mg/L

| hydroperoxide concentration, ppm | | | | | | | | | | | | | | |
| 15 hr | | | 30 hr | | | 55 hr | | | 40 hr | | | 60 hr | | |
AO	SwRI	CLASS[a]	AO	SwRI	CLASS[a]	AO	SwRI	CLASS[a]	AO	NIPER	CLASS[a]	AO	NIPER	CLASS
D	0.0	pass	D	1.0	pass	C	2.6	pass	B	1.2	pass	B	2.0	pass
B	0.6[b]	pass	H	2.0	pass	H	4.4	pass	E	1.3	pass	E	2.2	pass
L	1.4	pass	B	2.3[b]	pass	B	6.8	pass	C	1.6	pass	H	2.4	pass
C	2.3[b]	pass	C	2.6	pass	E	7.3	pass	A	1.6	pass	A	2.7	pass
F	2.9	pass	E	2.9	pass	D	7.8	pass	F	1.8	pass	F	3.5	pass
E	2.9[b]	pass	A	4.0	pass	F	9.0	margn	H	1.8	pass	C	4.1	pass
M	2.9	pass	F	5.8[b]	pass	A	10.2	fail	D	2.2	pass	D	4.2	pass
H	3.2[b]	pass	L	6.3	pass	G	16.8[b]	fail	G	3.8	pass	G	7.0	pass
A	3.6	pass	M	7.3	pass	M	22.1	fail	M	3.8	pass	M	8.2	margn
G	4.0	pass	G	8.4[b]	margn	N	33.6	fail	L	4.2	pass	L	12.3	fail
J	5.3	pass	I	8.4[b]	margn	L	43.6	fail	I	5.8	pass	N	16.7	fail
N	6.8	pass	N	10.9	fail	I	46.2[b]	fail	N	8.2	margn	I	25.1	fail
I	8.4	margn	J	15.2	fail	J	46.2	fail	J	14.2	fail	J	60.5	fail
NONE	28.1	fail	NONE	640	fail	NONE	2294	fail	NONE	150[c]	fail	NONE	150[c]	fail

a Classification of the fuels with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1-10.0 ppm; and fail = 10.0 ppm and above.

b Calculated estimate; c Value for 25 hr stress period: peroxidation data for longer stress duration not available.

Table 15C

Ranking and Classification of Antioxidants Screened at Three Stress Temperatures/Durations Indicated and at 240 kPa (35 psia) Oxygen

Based on Stress Tests Performed at NIPER and SwRI

In Fuel 18497 at 17 mg/L

AO	65°C[a] NIPER	100°C[a] SwRI		100°C[a] NIPER		120°C[a] SwRI		Rank[b]	Classification		
	161 dy	30 hr	55 hr	40 hr	60 hr	8 hr	12 hr		Pass	Margn	Fail
B	2 pass	3 pass	3 pass	1	1 pass	4 pass	1 pass	1	6	0	0
H	1 pass	2 pass	2 pass	6	3 pass	2 pass	3 pass	2	6	0	0
E	3 pass	5 pass	4 pass	2	2 pass	5 pass	4 margn	3	5	1	0
F	4 pass	7 pass	6 margn	5	5 pass	1 pass	2 pass	4	5	1	0
C	5 pass	4 pass	1 pass	3	6 pass	7 pass	8 fail	5	5	0	1
D	7 pass	1 pass	5 pass	7	7 pass	6 pass	7 fail	6	5	0	1
A	6 pass	6 pass	7 fail	4	4 pass	3 pass	5 fail	7	4	0	2
G	8 fail	10 margn	8 fail	8	8 pass	8 pass	6 fail	8	2	1	3
M	9 fail	9 pass	9 fail	9	9 margn	10 fail	9 fail	9	1	1	4
L	10 fail	8 pass	11 fail	10	10 fail	9 fail	10 fail	10	1	0	5
I	12 fail	11 margn	12 fail	11	12 fail	12 fail	12 fail	11	0	1	5
N	13 fail	12 fail	10 fail	12	11 fail	11 fail	11 fail	12	0	0	6
J	11 fail	13 fail	13 fail	13	13 fail	13 fail	13 fail	13	0	0	6
NONE[c]	103ppm[d]*	640 ppm	2294 ppm		150 ppm[e]*	2905 ppm f*					

a For these stress conditions, the fuels are classified with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

b Based on the antioxidant's overall effectiveness as described on p.14, in conjunction with its average ranking.

c Hydroperoxide concentration of the neat fuel at stress conditions specified, unless otherwise indicated.

d For 65 dy/65°C; e for 25 hr/100°C; f for 8hr/120°C; * peroxidation data for longer stress period not available.

Table 16
Overall Evaluation of Antioxidants Screened at Three Stress Temperatures*
Based on Ranking and Classification Average
For Both Fuels: 18496 and 18497

AO (17 mg/L)	Average Ranking and Classification[a] For:											
	Fuel 18496 (3 Tests)				Fuel 18497 (6 Tests)				For Both Fuels: 18496 and 18497 (Total of 9 Tests)			
	Rank	Pass	Margn	Fail	Rank	Pass	Margn	Fail	Rank[b]	Pass	Margn	Fail
B	3	2	1	0	1	6	0	0	1	8	1	0
H	2	2	0	1	2	6	0	0	2	8	0	1
E	4	2	1	0	3	5	1	0	3	7	2	0
F	5	2	1	0	4	5	1	0	4	7	2	0
A	1	3	0	0	7	4	0	2	5	7	0	2
C	6	1	1	1	5	5	0	1	6	6	1	2
D	8	0	1	2	6	5	0	1	7	5	1	3
G	7	1	0	2	8	2	1	3	8	3	1	5
M	9	0	0	3	9	1	1	4	9	1	1	7
L	10	0	0	3	10	1	0	5	10	1	0	8
I	12	0	0	3	11	0	1	5	11	0	1	8
N	11	0	0	3	12	0	0	6	12	0	0	9
J	13	0	0	3	13	0	0	6	13	0	0	9

* Based on stress tests performed at SwRI and NIPER.

[a] Fuels are classified with respect to the military specification limit of 8.0 ppm hydroperoxides, where: pass = 8.0 ppm or less; margn (marginal) = 8.1- 10.0 ppm; and fail = 10.0 ppm and above.

[b] Based on the antioxidant's overall effectiveness as described on p.14, in conjunction with its average ranking.
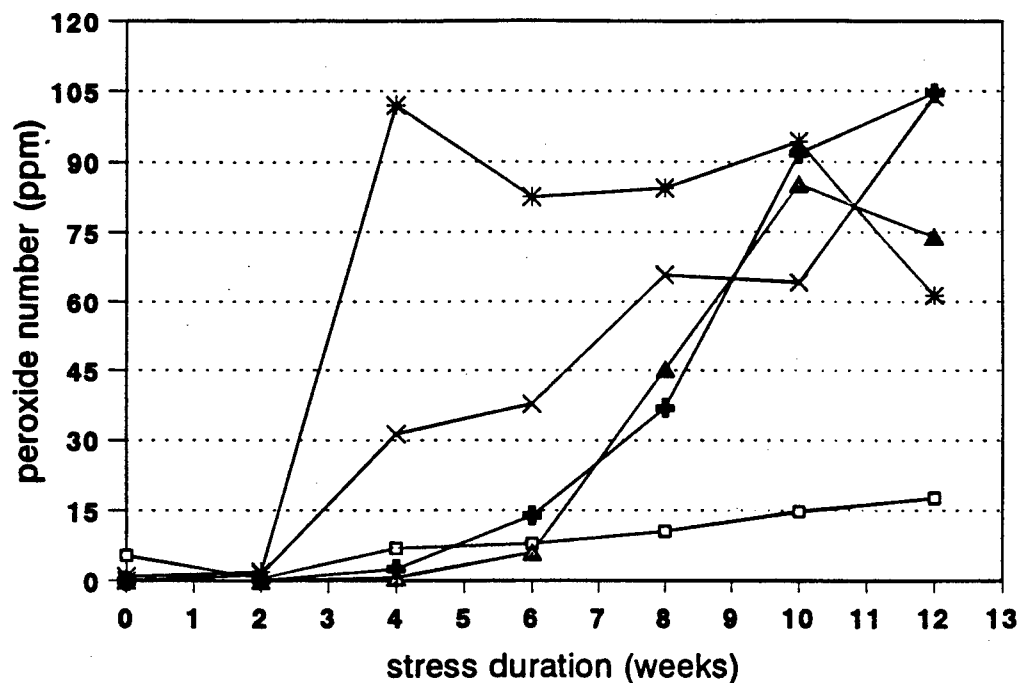
Figure 1. Hydroperoxides formed in CAPPED bottles at
65 °C/atmospheric pressure/12 weeks.
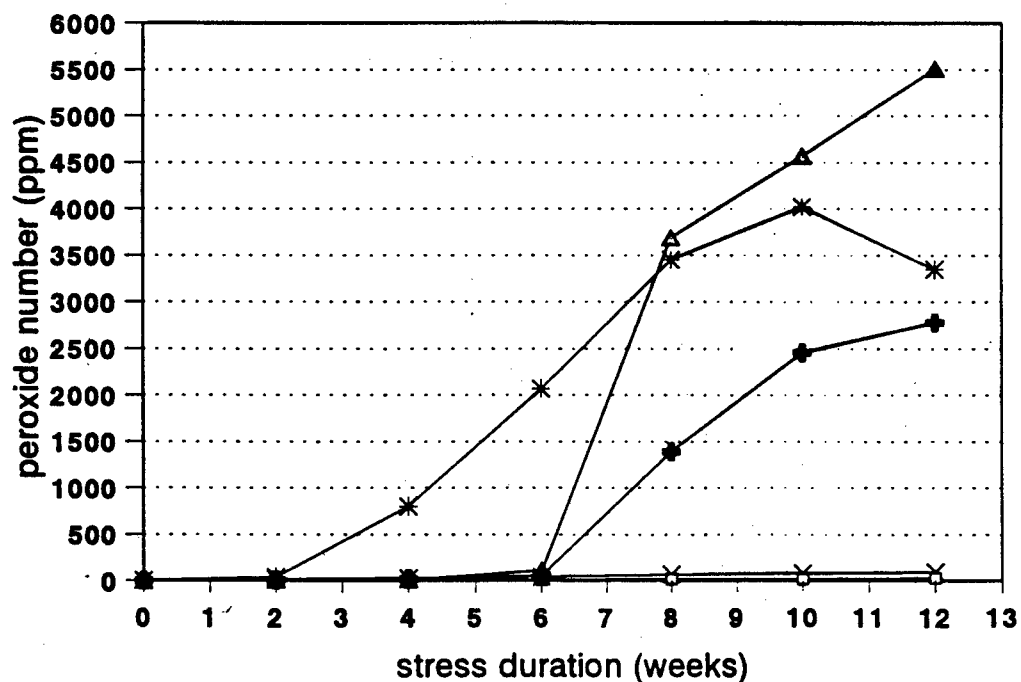
Figure 2. Hydroperoxides formed in VENTED bottles at
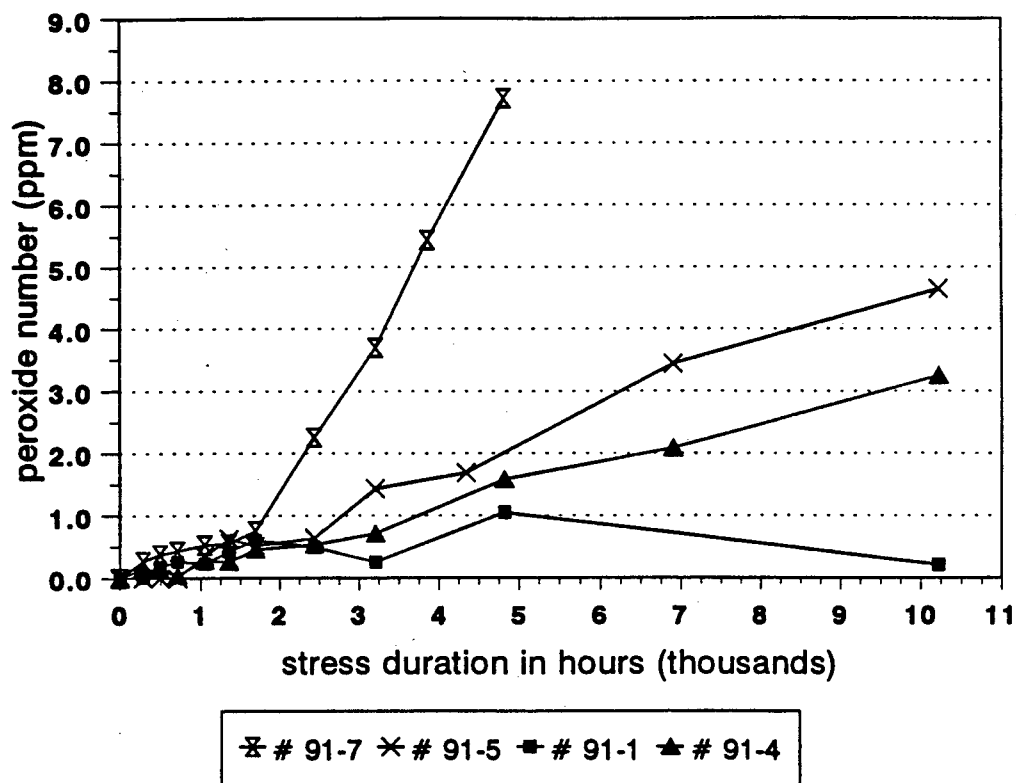65 °C/atmospheric pressure/12 weeks.

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Figure 3. Accelerated storage stability at 50 °C/atmospheric pressure for 4 current production additive-free fuels.
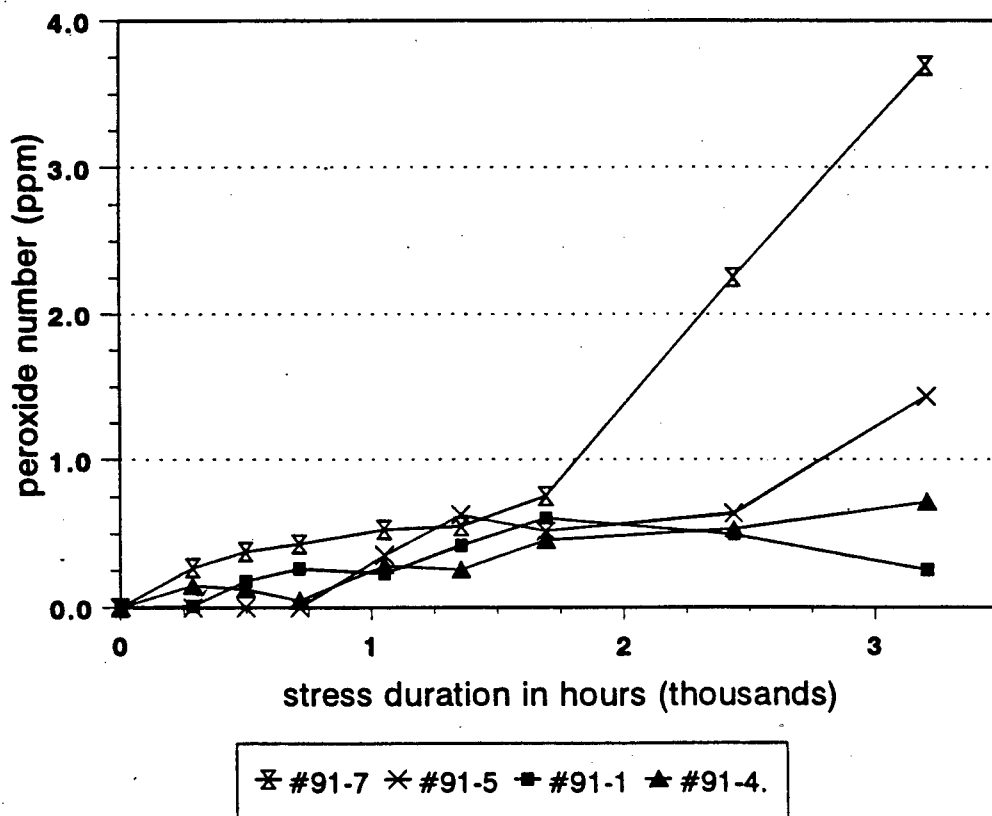

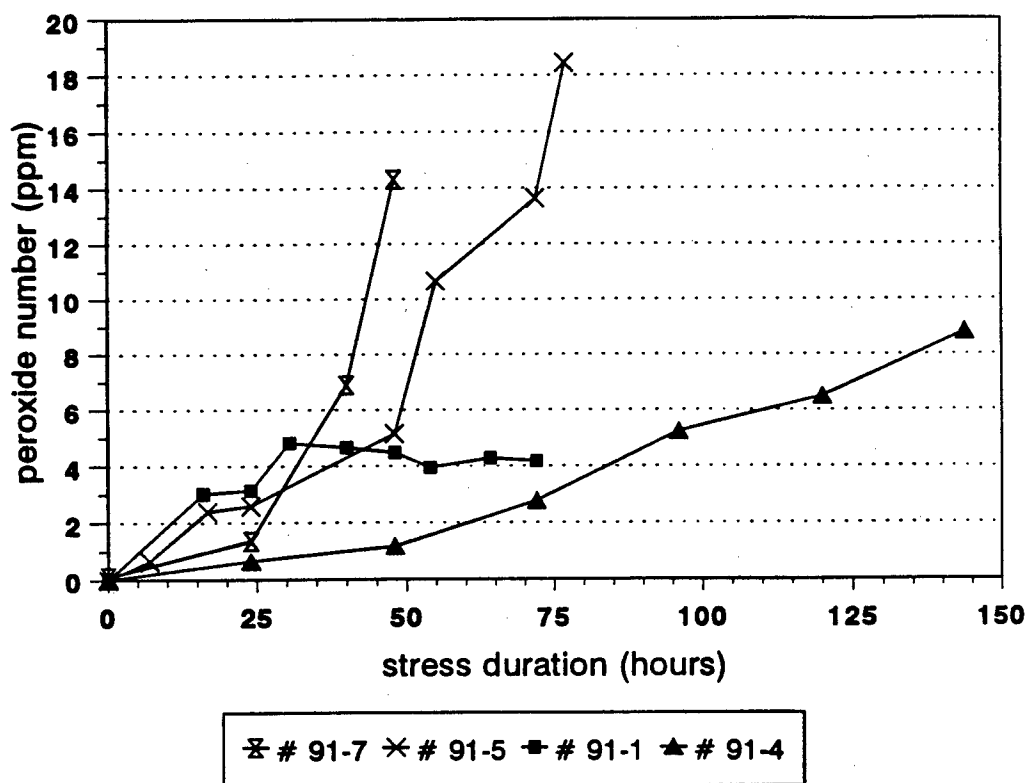Figure 3A. Expanded ordinate of figure 3.

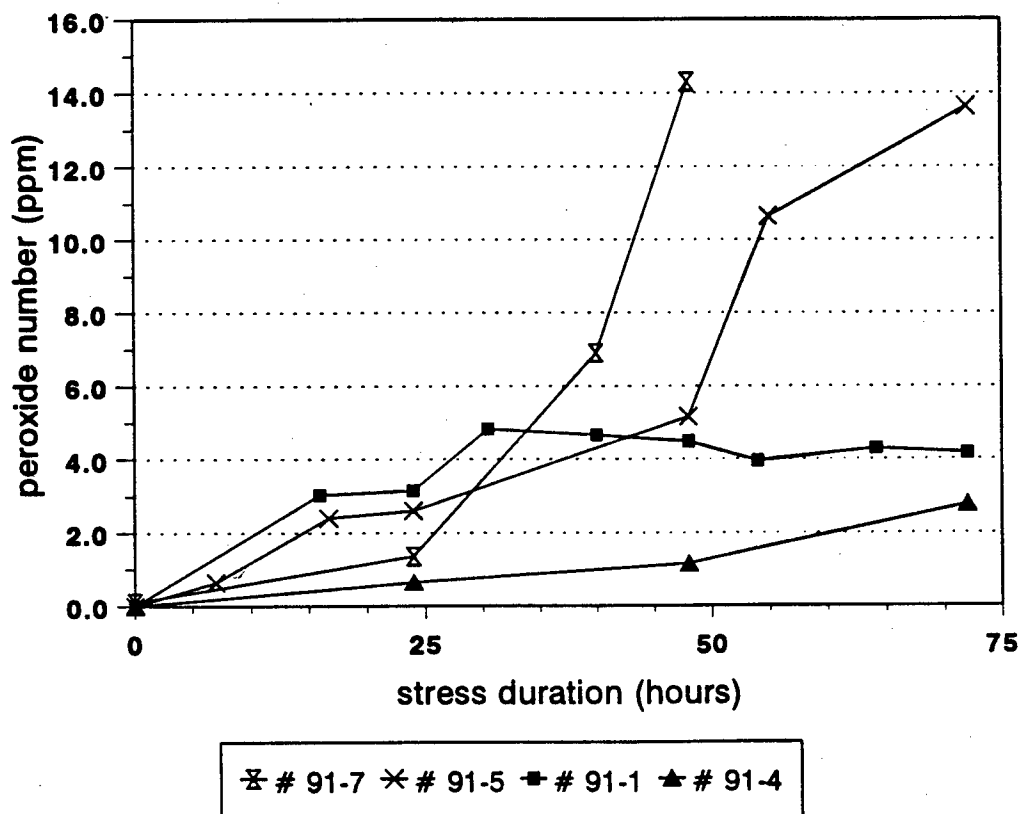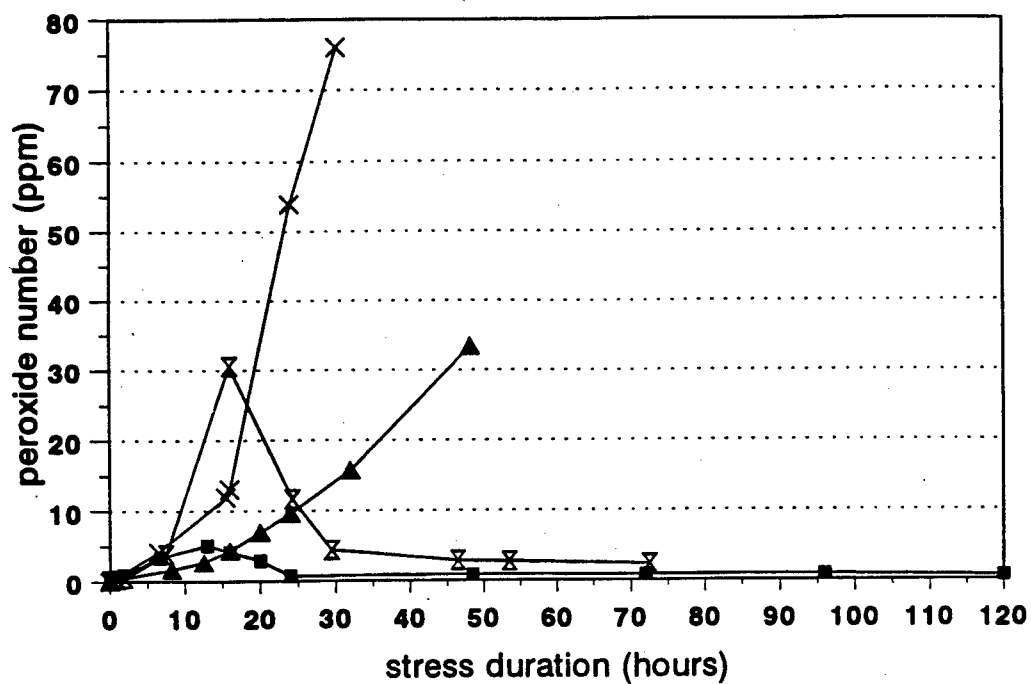Figure 4. Accelerated storage stability at 100 °C/atmospheric pressure for 4 current production additive-free fuels.
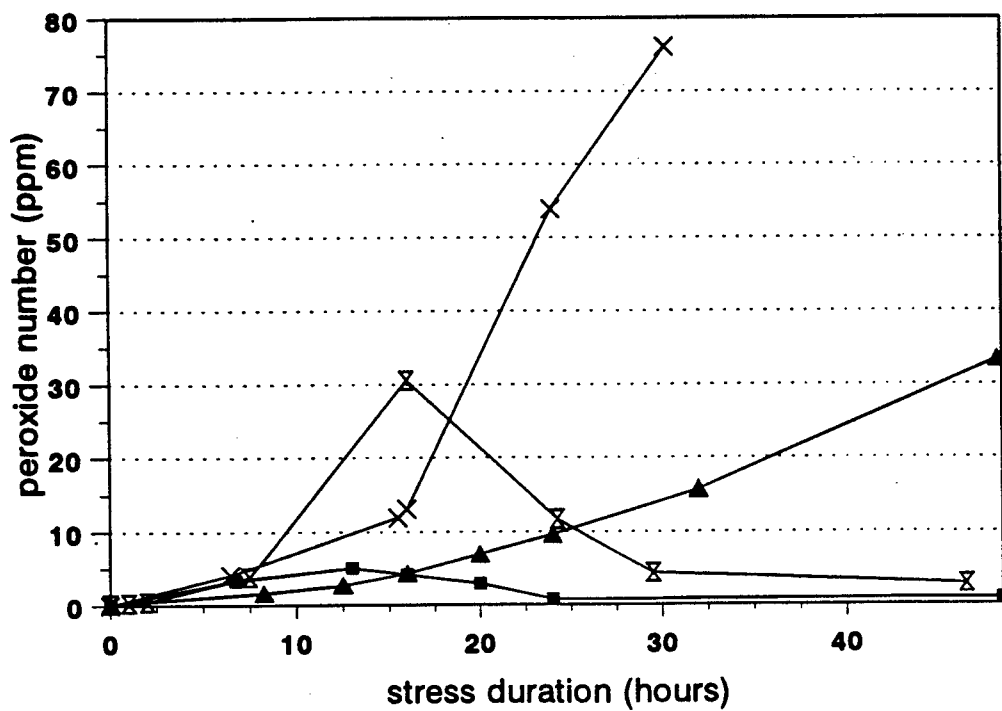

Figure 4A. Expanded ordinate of figure 4.

Figure 5. Accelerated storage stability at 120 °C/atmospheric pressure
for 4 current production additive-free fuels.

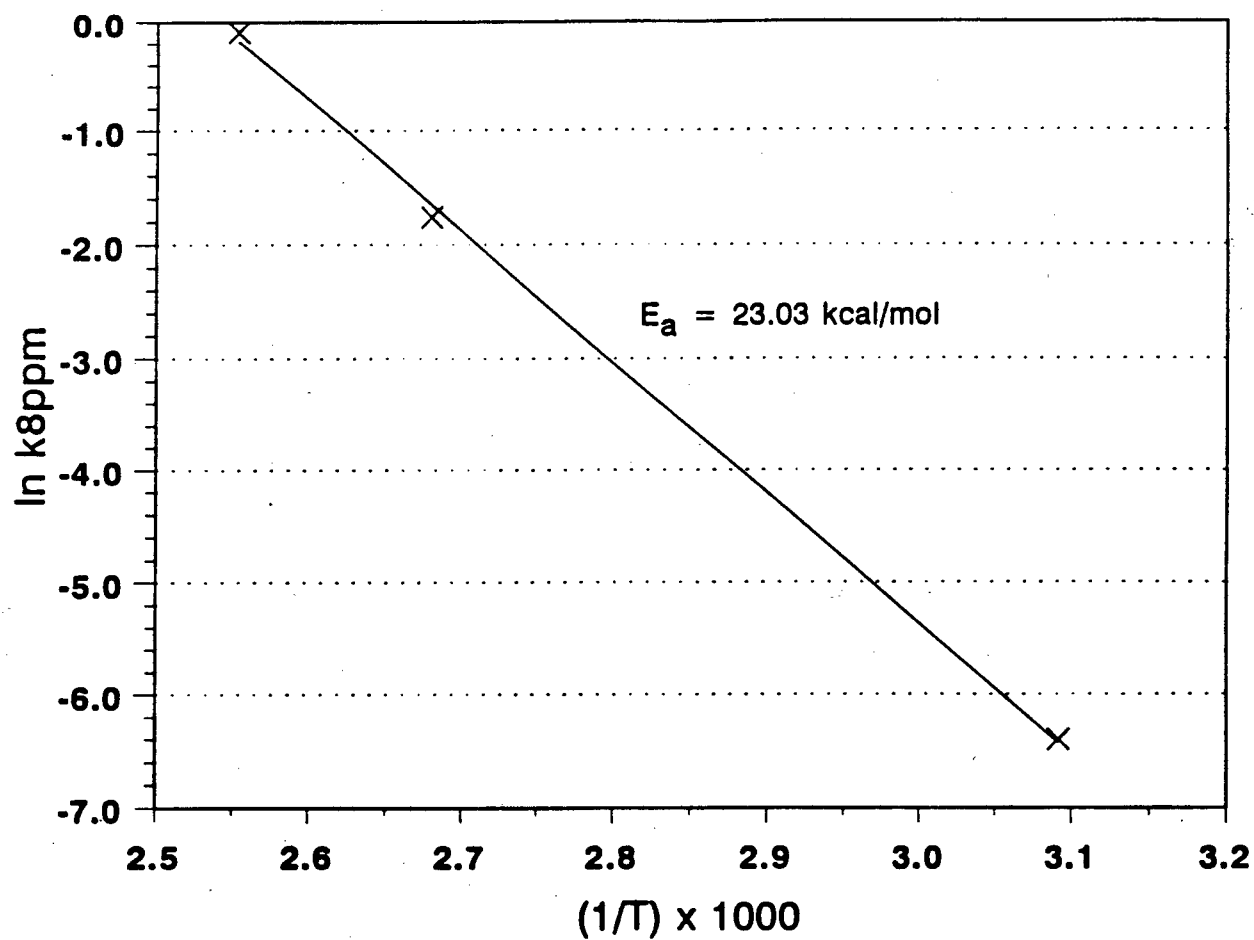Figure 5A. Expanded ordinate of figure 5.

Figure 6. Arrhenius plot based on rate to attain 8 ppm ROOH at 50 °C, 100 °C, and 120 °C/atmospheric pressure for fuel 91-7.